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Absence of orbital currents in superconducting $YBa_2Cu_4O_8$ using a Zeeman-perturbed nuclear-quadrupole-resonance technique

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Zeeman perturbed nuclear quadrupole resonance was applied to evaluate weak magnetic fields in the context of orbital currents in cuprate superconductors. The magnetic environment of the barium atom in *c*-axis oriented powder samples of $YBa_2Cu_4O_8$ was investigated in the pseudogap phase at 90 K. No evidence for orbital currents was found: Any static and dynamic field must be less than 0.07 mT and 0.7 mT respectively.

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Presumed orbital currents (OCs) (*e.g.* [1, 2]), emerging in the Hubbard model, have been proposed to explain the pseudogap of the cuprate superconductors [3]. Support for OCs was found *e.g.* in [4], a computer simulation, but several other theoretical investigations [5–7] have not confirmed the suppositions put forward. As for experimental evidence, the state of affairs appears likewise to be ambiguous. While some recent work using spin-polarized inelastic neutron scattering report magnetic signatures that were interpreted as OCs [8–12], a later muon spin rotation study on the very same sample [13] attributes these rather to magnetic impurity phases. Angle-resolved photoemission spectroscopy [14] also reveals features that were suggested to indicate OCs, but the data are presently regarded as controversial [15]. The current state of knowledge about OCs is thus contradictory. Local magnetic fields must inevitably arise from OCs, but no evidence for additional fields was found using yttrium nuclear magnetic resonance (NMR) [16] and muon spin rotation [13, 17], despite the pronounced sensitivity of these direct methods for weak local magnetic fields.

In this paper, we specifically address two issues with an experiment of novel design, and seek an exchange of arguments with theory. Our first concern is the choice of atomic site where fields should be determined. The Y atom occupies a position between the two copper oxide planes of a cuprate bilayer. For the circulating current (CC) pattern [2], OCs in the two planes might reduce the field that is effectively sensed at the yttrium site. The Ba atom, though, is situated outside, but close to the bilayer, at a position where the combined fields from the two neighboring layers would be enhanced because of the suggested ferromagnetic order [9, 10] of moments within the bilayer. We report here that we did not find any trace of additional local fields at the Ba site.

The small nuclear magnetic moment of the spin $I=\frac{1}{2}$, spherically symmetric ^{89}Y nucleus can be used as sensor for local magnetic fields only if the degeneracy of magnetic energy levels is removed with an external magnetic field (of order Tesla), as is the working principle of NMR. We acknowledge as an open question whether this strong field could have an influence on the circulation of OCs. In contrast, the *Zeeman perturbation* technique utilizes the fact that the Ba atom has both a quadrupolar and a nuclear magnetic moment. This technique is a rarely implemented variant of nuclear quadrupole resonance (NQR), which utilizes the local electric field gradient to lift the nuclear degeneracy, and does not require a strong magnetic field.

Polycrystalline stoichiometric $YBa_2Cu_4O_8$ of 98% phase purity ($T_c \approx 81$ K) was prepared with a technique described elsewhere [19]. The sample is inherently underdoped [20] and exhibits a pronounced pseudogap. Chemical homogeneity ensures narrow NQR resonance lines. The intensity of the NQR signal of Ba was enhanced by isotope enrichment, 44% ^{135}Ba and 46% ^{137}Ba. Contamination of Ba resonance signals from ^{63}Cu was minimized through a 99.6% ^{65}Cu enrichment. In order to make the angular dependence of the local field accessible, samples were *c*-axis oriented in a static 9 T magnetic field and cured at elevated temperatures in epoxy resin. The anisotropy of the normal state magnetic susceptibility sets up a torque that tends to preferentially orient the *c*-axis of the grains to the external field, while the *a*- and *b*-axes of the crystallites remain randomly distributed in a plane perpendicular to the *c*-axis.

A phase-coherent pulsed NQR spectrometer was employed for the measurements [18]. Essentially, the sample is exposed to a pair of NQR frequency pulses. The first pulse tilts the nuclear coherent spin magnetization, while the second detects the magnetization remaining in the spin ensemble after the pulse separation time τ. The resulting spin echoes were collected using alternating phase averaging. The evolution of the magnetization with τ depends on the local magnetic environment.

The Zeeman perturbation is introduced by means of an external coil as a weak static magnetic field (of order mT), below referred to as the *Zeeman field*, or B_{ext}. The nuclear magnetic moment of Ba interacts through magnetic hyperfine coupling with any magnetic field present. Quantum mechanical calculations by Dean [21] show that for nuclei with $I = \frac{3}{2}$, as for ^{137}Ba, a weak magnetic field perturbs the quadrupole resonance and splits the pure NQR spectrum in four separate lines, in the literature commonly denoted α, α', β, and β'. For ^{137}Ba in $YBa_2Cu_4O_8$, with a resonance frequency $^{137}\nu_Q \approx 31$ MHz at room temperature, the line split in the presence of a field of the order of mT is typically a few kHz. The intensities and frequencies of the lines depend on the angle θ of the applied field with respect to the quantization axis, for NQR defined by the electric field gradient. For the purpose of the present experiment, it is important to keep in mind that for $B_{\rm ext} \parallel c$ ($\theta = 0°$) the α-transitions dominate, whereas for $B_{\rm ext} \perp c$ ($\theta = 90°$) all four transitions are present [18, 21]. The amplitude of the pulsed radio frequency pulses is much larger than any intrinsic local field, and thus all transitions excited.

For a typical ^{137}Ba NQR resonance line of a few hundred kHz width, see inset of Fig. 1, the line split caused by a field of the order of mT is not directly observable, which is where Zeeman perturbed NQR becomes useful. The principle of the measurement is to detect an additional magnetic field $B_{\rm loc}$ through a *beat oscillation* with frequency $\omega_{\rm loc} = \gamma_n B_{\rm loc}$ superposed on the Gaussian shaped decay of the spin echo intensity with τ, as in Fig. 1. The reader is referred to the literature for details [18, 22]. In brief, the beat oscillation corresponds to the magnetic field splitting of the pure quadrupole states, thus offering enhanced sensitivity for local weak magnetic field.

The detected spin echo intensity may be analyzed for $B_{\rm loc}$ with the following expression [23], taking into account the beat frequency $\omega_{\rm loc}$:

$$I(2\tau) = I_0 \exp\left(-\frac{1}{2}\,(\frac{2\tau}{T_2})^2\right) \times \times \left[1 - K \exp(-\frac{2\tau}{T_2'}) \cdot \cos(2\tau\,\omega_{\rm loc} - \varphi)\right]. \tag{1}$$

Here I_0 is the initial spin echo intensity; the phase shift φ depends on the pulse scheme applied and the local magnetic field. The exponential prefactor invokes an effective spin-spin relaxation time T_2', which takes into account the damping due to any slight misalignment of c-axis of the grains; the parameter $K \approx 1$ accounts for any magnetic field that may reduce the full excitation of the split resonance of Ba nucleus.

For a general NQR investigation there is no additional field $B_{\rm loc}$. The distribution of homonuclear dipolar fields at the Ba site results in a Gaussian exponential decay of the spin echo intensity I_0 with pulse separation time τ, characterized by the spin-spin relaxation rate T_2^{-1}. Only the first exponential factor of Eq. (1) is required to describe this situation.

In order to demonstrate the sensitivity of the technique for weak local magnetic fields, the Ba site was studied at 300 K, where no OCs would be expected, and consequently no additional magnetic field should be observed. The result of this measurement is presented in Fig. 1, revealing the expected dominating Gaussian decay of the spin echo intensity with pulse separation time τ in agreement with previous studies [24]. This curve is our zero-field reference.

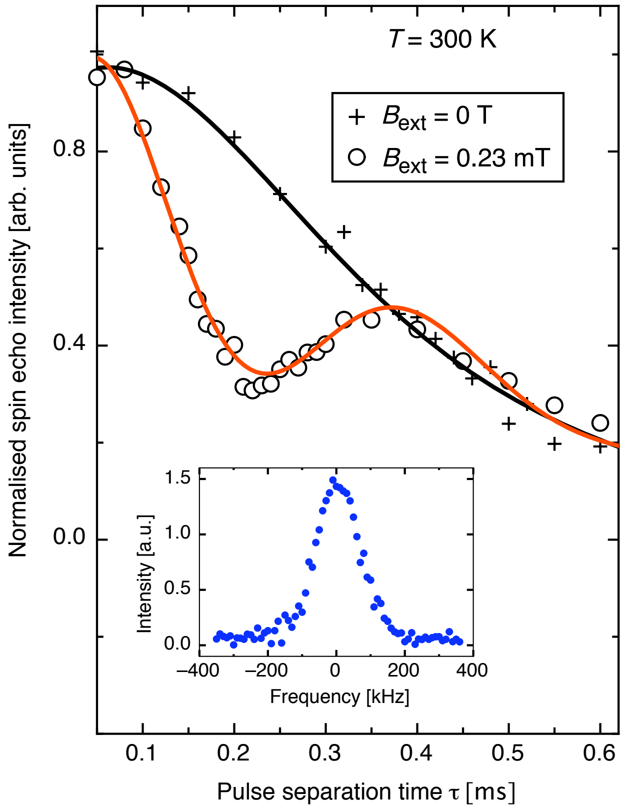

FIG. 1: (Color online) Normalized ^{137}Ba spin echo intensity at 300 K parallel to the c-axis in $YBa_2Cu_4O_8$ in dependence of the pulse separation time τ. Results for zero field and for $B_{\rm ext} = 0.23$ mT. Solid lines were fitted to data with Eq. (1), see text. Inset shows ^{137}Ba resonance line at 30.9 MHz, no external field, 300 K.

The experiment was then repeated at the same temperature with an arbitrary Zeeman field $B_{\rm ext} = 0.23$ mT applied parallel to the c-axis. In effect, a local field $B_{\rm loc}$ is simulated with the applied field $B_{\rm ext}$. The τ-dependence of the decaying spin-echo intensity now shows a distinct response to the applied field through the modulation, indicating a significant sensitivity to weak local fields of the order of μT. In Fig. 1 the solid lines were obtained by fitting both data sets to Eq. (1), resulting in $B_{\rm loc} = 0.07(3)$ and 0.28(3) mT for measurements with applied Zeeman fields 0 mT and 0.23 mT respectively. Moreover, we found $T_2(300\,{\rm K}) = 0.92(5)$ ms, in accord with [24].

The actual measurement should reveal the presence of

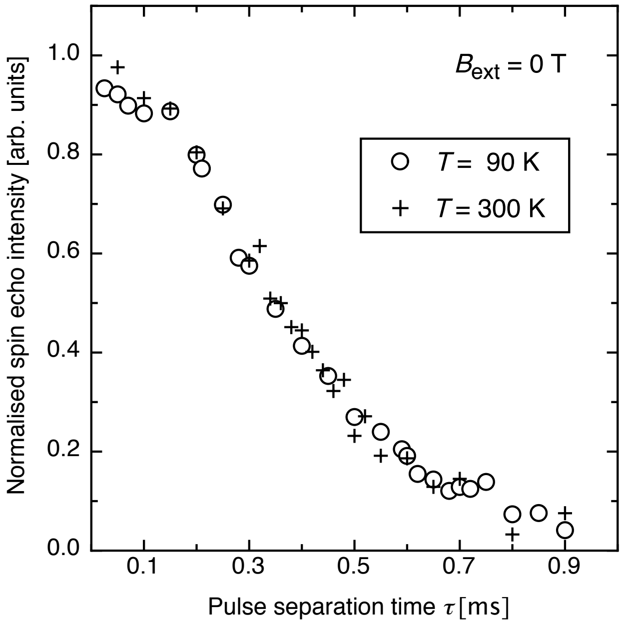

FIG. 2: (Color online) Spin echo intensity decay with pulse separation time τ for zero field at 300 K and 90 K. No distinguishable change in the normalised intensity was detected in the pseudogap phase.

a weak intrinsic local field in the pseudogap phase at 90 K. With no Zeeman field applied, *i.e.* $B_{\rm ext} = 0\,$mT, we obtained the data shown as open circles in Fig. 2. A comparison with the reference measurement at 300 K, repeated in the figure, confirms an essentially temperature independent spin-spin relaxation process [24]. Furthermore, any intrinsic field unfolding in the pseudogap phase, with a c-axis component larger than the detection limit, should be visible as a deviation from the reference measurement in the form of beat oscillations. Evidently, the two data sets are indistinguishable, which we cannot explain other than by the absence of an additional static field in the pseudogap phase.

It remains to establish a calibration of the procedure, and to determine the detection limit in the pseudogap phase at 90 K. For this purpose, different Zeeman fields $B_{\rm ext}$ of known strength were applied and the beat signatures analyzed for both orientations of the c-axis. Results in Fig. 3 show best simultaneous fits of Eq. (1) to the entire set of measurements for each orientation. Fields $B_{\rm loc}$ thus determined, were found to deviate less than 0.07 mT from the Zeeman fields $B_{\rm ext}$ applied with the calibrated external coil. In all experiments, background contributions, including Earth's magnetic field, were shielded so as to contribute less than 0.5 μT.

For the zero field data the simultaneous fits yielded for both orientations $B_{\rm loc}\approx$ 0.05 mT, which by simple trigonometric arguments translates to an effective detection limit for local fields less than $\sim$0.07 mT in any crystallographic direction.

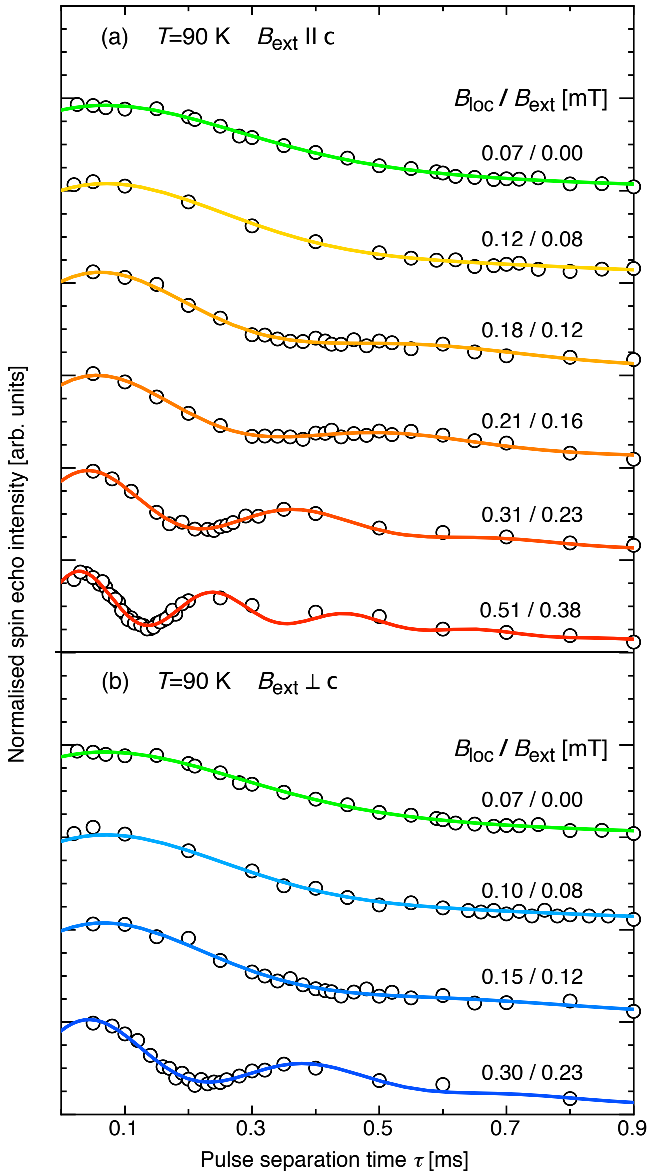

FIG. 3: (Color online) Normalized spin echo intensity decay with the pulse separation time τ for some applied external fields $B_{\rm ext}$, at $T = 90\,$K, for ^{137}Ba in $YBa_2Cu_4O_8$. The corresponding fields $B_{\rm loc}$ were calculated by fitting Eq. (1) to the data, see text. Experimental data are represented by open circles; fitted results by solid lines. Panel (a) shows data and results for magnetic fields $B_{\rm ext}$ = 0, 0.08, 0.12, 0.16, 0.23, and 0.38 mT applied parallel to the crystalline c-axis; panel (b) for $B_{\rm ext}$ = 0, 0.08, 0.12, and 0.23 mT applied perpendicular to the c-axis. Data sets were shifted vertically for clarity. Field strengths are given next to each curve.

Since any contributions of magnetic fields add as vector components, the result excludes that a large intrinsic magnetic field could be present. We confirmed this by applying $B_{\rm ext}$ also perpendicular to the c-axis. The electric field gradient at the Ba site is not axially symmetric

[24], from which follows that the quadrupole line split observed represents a distribution. The details of this are beyond the scope of this paper, and we refer again the reader to [18, 21]. For the present purpose, it suffices to know that for $\theta = 90^\circ$ the ensuing additional distribution of frequencies leads to a broadening of the leading minimum in the spin echo intensity decay, compared with the case for $\theta = 0$, but without any noticeable shift of the position of the leading minimum. Although the evaluation procedure, as described, determines the high sensitivity of the present evaluation, the general conclusion does not rely upon it: Calculating the local field directly from $B_{\mathrm{loc}} = \pi/2\tau\gamma_{\mathrm{n}}$, using the τ-value of the leading minimum, results in satisfactory results for fields higher than 0.16 mT.

Finally, we considered local fluctuating fields generated by possible non-static OCs. Spin-lattice relaxation is sensitive to magnetic fields fluctuating perpendicular to the quantization axis. Following an evaluation procedure equivalent to that in [16], we estimated the maximum of the fluctuating field amplitude from ^{137}Ba NQR spin-lattice relaxation measurements. The magnetic signatures observed with neutron scattering [12] were reported not to change while cooling through T_{c}, indicating that any magnetic features ascribed to the pseudogap must coexist with superconductivity. Since fluctuations become slower as temperature decreases, we chose to determine the relaxation time at 8 K in order to attain high sensitivity ($^{137}T_1 = 216(9)\,\mathrm{s}$). No oscillation in the τ-dependence of the spin echo intensity decay was observed, from which we conclude that no static field is present, and therefore any field at 8K must be dynamic in nature. In order to estimate the maximum fluctuating field amplitude that may be attributed to OCs, we conservatively assigned the observed relaxation rate at 8 K entirely to OCs, *i.e.* $^{137}T_1^{-1} \equiv (^{137}T_1^{\mathrm{orb}})^{-1}$.

Bloembergen-Purcell-Pound relate spin lattice relaxation [25] to the time average (symbol ^{t}) of a fluctuating field amplitude, here assumed to be ΔB_{orb}, and the correlation time τ_{c} [25, 26] as follows:

$$\frac{1}{^{137}T_1^{\mathrm{orb}}} \approx \overline{^{137}\gamma_n^2 \cdot \Delta B_{\mathrm{orb}}^2}^{\,t} \cdot \frac{\tau_{\mathrm{c}}}{1 + (2\pi\, ^{137}\nu_{\mathrm{Q}}\, \tau_{\mathrm{c}})^2} \quad , \qquad (2)$$

where $^{137}\nu_{\mathrm{Q}}$ is the NQR frequency. Assuming the value $\tau_{\mathrm{c}} \leq 10^{-11}$s from a neutron scattering investigation [9], as the upper limit for fast fluctuating OC field amplitudes, ΔB_{orb} at the Ba site in $\mathrm{YBa_2Cu_4O_8}$ was estimated to be less than $\sim$0.7 mT at 8 K.

Literature provides no theoretical predictions for local fields at the Ba atom site. Our straightforward point dipole field calculations for a CC pattern [2, 27] decorated with 0.1 μ_{B} [10], suggests a local field strength of 7 mT ($\perp c$), which is *two orders* of magnitude above our limit of detection of 0.07 mT. For comparison, a field strength of 29 mT was calculated [28] for the almost equivalent apical oxygen site. For the DDW pattern, using 0.0025 μ_{B} (from [8]), our dipole calculation yield 0.7 mT $\parallel c$ at the Ba site (one order of magnitude above our detection limit).

In conclusion, the results presented do not indicate the presence of additional local fields at the Ba site in the pseudogap phase of c-axis oriented $\mathrm{YBa_2Cu_4O_8}$. The detection limit of our method allows static or dynamic field less than 0.07 mT and 0.7 mT respectively. In particular, these results appears not to be consistent with previously reported interpretations of magnetic signatures observed with inelastic neutron scattering [8–12]. Our findings are supported by thorough theoretical investigations, such as [5, 6] (exact diagonalization), [7] (density-matrix renormalization group).

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